A STUDY OF COBALT IN SOILS

BY

DILIP KUMAR BANERJEE

B.Sc., Calcutta University, 1943
B.S., Cornell University, 1947
M.S., Cornell University, 1948

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN AGRONOMY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1952

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Introduction

Cobalt may be classed with those elements which are essential for animal and human health but which are not required by plants. Pioneer research in Australia and New Zealand has established quite clearly that certain deficiency diseases produced in ruminants were due to a lack of cobalt in the feed available to the animals. However, attempts to relate the low cobalt content of plants to the total cobalt content of soils were not successful.

It is now known that the uptake of an element by plants is dependent upon the available forms of that particular element and not upon the total amount present in the soil. Since very little work has been done on the chemistry of cobalt in soils, the objectives of this study were (1) to determine the nature of the forms which cobalt assumed when added to soils and clays, (2) to determine what extracting solutions would be suitable for extracting these forms from the soil, and (3) to survey the cobalt status of some Illinois soils and determine which of the soil forms was most closely related to the cobalt content of plants. Such a form, or forms, would then be available to the plant.

Methods

In order to study the behavior of cobalt added to soils and clays, radioactive cobalt was used as a tracer. In experiments where small amounts of cobalt were added, the radioactive form was the only source of the element. When large amounts of cobalt were required, an isotope dilution technique employing large amounts of inactive cobalt and a negligible amount of radioactive cobalt was used. The extracting solutions used in these experiments were neutral normal ammonium acetate, 2.5 per cent acetic acid at pH 4.5, 0.1 N HCl and 2N HCl.

In the survey of some representative Illinois soils, the colorimetric nitroso-R-salt method with some modifications to increase its sensitivity was used for cobalt determinations in soil extracts and plant material. The methods of extraction and analysis are discussed and described in detail.

Results

When 5 ppm of radioactive cobalt were added to each of a series of soils with pH values ranging from 5 to 8.3, the cobalt distributed itself in fractions extractable with ammonium acetate, 2.5 per cent acetic acid and 0.1 NHCl. The ammonium acetate fraction decreased rapidly with increase in pH of the samples. This relation was shown by a regular curve.

In hydrogen-saturated clays and soils with pH values ranging from 2.7 to 3.2, essentially all the absorbed cobalt was extracted by a single leaching with ammonium acetate. There was essentially no acid-extractable cobalt in these systems.

In calcium-saturated clays and soils which had pH values of 8.0, the acid-extractable fraction of cobalt increased considerably. A single rapid leaching with 0.1 N HCl did not completely remove this fraction. An increase in the time of contact between the HCl and the sample resulted in almost complete extraction of the acid-extractable form.

The fraction of cobalt extracted by ammonium acetate was shown to be an exchangeable form. Extractions made with 1N $NaNo_3$ gave results that agreed very closely with those of the ammonium acetate extractions. This form of cobalt should therefore be expected to behave like the other common exchangeable cations.

There was a possibility that 0.1 N HCl was extracting insoluble salts of cobalt; however, experiments showed that there was a reduction in the exchange capacity of calcium-saturated samples to which cobalt had been added. This reduction in capacity agreed very colsely with the amount of acid-extractable cobalt found, indicating that this form of

cobalt was a strongly-adsorbed rather than a precipitated form.

The strongly-adsorbed form of cobalt did not form immediately after the addition of cobalt. In a sample of calcium-saturated illite, all the absorbed cobalt was exchangeable if extractions were made within 15 minutes of the cobalt addition. Part of the exchangeable cobalt changed to the strongly-adsorbed form with the passage of time. This transformation was virtually complete at the end of 10 days.

The ease of release, or "f" value, of cobalt in simple exchange in hydrogen-saturated soils and clays was determined. The position of cobalt with respect to the other exchangeable cations whose "f" values have been determined by Bray, is as follows:

Na^+		K^+		Mg^{++}		Ca^{++}		Co^{++}		H^+
6.2	>	2.3	>	1.6	>	1.0	>	0.69	>	0.35

This "f" value for cobalt does not apply to calcium-saturated systems where the exchange reaction is no longer simple.

The following conclusions were drawn from a survey of the cobalt status of six representative Illinois soils.

1. The total cobalt varied from about 5 to 8 ppm.

2. The exchangeable cobalt varied from 0.01 to 0.35 ppm.

3. Acid-extractable cobalt varied from 1.0 to 2.65 ppm.

The differences in the levels of this form of cobalt at the different locations were statistically significant.

4. The largest proportion of the total cobalt was found to exist in forms that could not be extracted by dilute acids.

5. The relation between pH of the soils and the amounts of exchangeable and acid-extractable cobalt in the soils was very similar to that found in the tracer experiments.

6. The levels of cobalt in the plant material used in these experiments were found to be very low and approaching the

levels of deficiency established in other parts of the world. The values for the untreated soils ranged from a low of 0.019 ppm to a high of 0.190 ppm.

7. Exchangeable cobalt in the soil appeared to be the form most available to plants, although the linear correlation coefficient was not significant.

8. There was no apparent relationship between the cobalt content of plants and the acid-extractable or total cobalt in these soils. The linear correlation coefficients were not significant.

VITA

The author was born on June 7, 1923 in Edinburgh, Scotland. He received his secondary school education at St. Xavier's School, Calcutta, India and was graduated in December, 1939 with the University of Cambridge School Certificate.

He entered St. Xavier's College, Calcutta in January, 1940 and received the University of Cambridge Higher School Certificate in January, 1941. Continuing at the same institution, he obtained a Bachelor of Science degree with honors in Physics in May, 1943.

He entered Cornell University in the fall of 1945 and was awarded a Bachelor of Science degree in June, 1947. He enrolled in the Graduate School there in September, 1947 and obtained a Master of Science in Soils with a minor in Plant Physiology in September, 1948. He was admitted to the Graduate College of the University of Illinois the same year and was appointed an Assistant in Soil Fertility in April, 1949.

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